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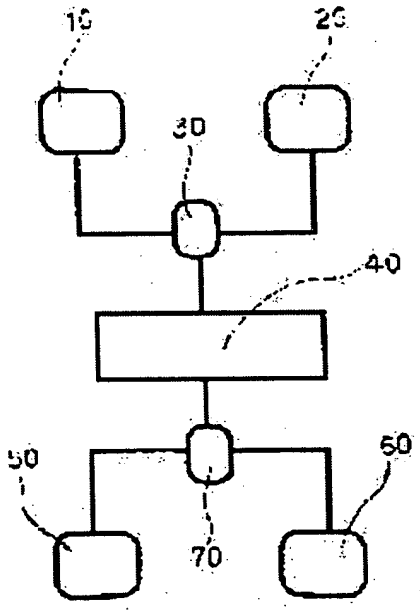
(54) MANUFACTURE OF REACTIVE INJECTION FOAMED MOLDED PRODUCT

(57)Abstract:

PURPOSE: To manufacture a reactive injection foam molded product of uniform thickness and density of a skin layer and of good product quality by injecting a non- foamable reactive composition raw liquid onto the foam molded surface in a mold and performing the reactive curing when the foam molded surface of the foamable reactive composition raw liquid is in the semi-cured state.

CONSTITUTION: A foamable reactive composition raw liquid formed by collision mixing and injecting respective raw materials of raw material tanks 10 and 20 by a mixing head 30 is reacted and semi-cured in a molding die 40, and a foam molded body in the semi-cured state is formed by gas to be generated. When the above-said surface layer is in the semi-cured state, a non-foamable reactive composition raw liquid prepared by collison mixing respective raw materials in raw material tanks 50 and 60 by means of a mixing head 70 is injected onto the surface of the molded body in the molding die 40. Then the foam molded body in the semi-cured state is covered by the raw liquid and cooled starting from a section in contact with an inner wall face of the molding die 40, and a layer covered by a non-foamable reactive composition and the foam molded body in the semi-cured state are cured together integrally to form the foam molded body with a non-formable skin layer as a covering layer.



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CLAIMS

[Claim(s)]
[Claim 1] The manufacture approach of the reaction injection foaming article which is made to foam while injecting and carrying out reaction semi-hardening of the reactant constituent undiluted solution of fizz into the mold for shaping, and is characterized by injecting the reactant constituent undiluted solution of non-fizz into the front face of the foaming object in a mold, and carrying out reaction hardening when the surface layer of this foaming object is in a semi-hardening condition.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the manufacture approach of a reaction injection foaming article like integral skin foam.
[0002]
[Description of the Prior Art] Reaction hardening of the reactant constituent undiluted solution of fizz is injected and carried out into the mold for shaping, and the method of manufacturing a reaction injection foaming article like integral skin foam (form with a skin) is learned.
[0003] If it is in the manufacture approach of this kind of reaction injection foaming article, in order to improve the fluidity within the mold of a reactant constituent undiluted solution, heating maintenance of the mold for shaping is usually carried out at 30-60 degrees C. On the other hand, a reactant constituent undiluted solution generates heat at the time of reaction hardening, and becomes an elevated temperature (in for example, urethane foam shaping, it is about 100 degrees C) from whenever [mold temperature].
[0004] And it is cooled from the part which foams with reaction hardening and touches a mold, the gas in the cellular film formed in the part which touches a mold by that cause is cooled, and it condenses, and the cellular film of this part shrinks, the skin of high density is formed, and the reactant constituent undiluted solution of foaming agent content is cooled and unmolded to the temperature which can unmold those late-coming bubble mold goods.
[0005] However, when a foaming article is cooled in the condition of having been held at the constant temperature whose temperature of the mold for shaping is 30-60 degrees C in this way, lowering to the temperature which can unmold the temperature of the foaming article in a mold takes time amount, and productivity is low.
[0006] Moreover, comparatively thinly (about about 1mm), moreover the skin of the consistency formed is also comparatively small, its reinforcement is weak in the foaming article which is obtained for the reason, and a product satisfying enough is not obtained.
[0007] Then, in order to shorten time amount until it unmolds, to raise productivity and to obtain the foaming article of high intensity, after heating the mold for shaping to constant temperature and carrying out reaction hardening of the reactant constituent undiluted solution, the approach of controlling the thickness and the consistency of a skin is proposed by quenching this mold for shaping (refer to JP,63-24448,B).
[0008]
[Problem(s) to be Solved by the Invention] However, by the approach of the above-mentioned proposal, although the thickness of a skin increases, there is surely dispersion in temperature distribution in the mold for shaping, and since few air bubbles which originate in dispersion in these temperature distribution, and exist in a skin change delicately, the problem that the thickness and the consistency of a skin serve as an ununiformity has it.
[0009] The place which this invention solves the above-mentioned problem and is made into that purpose has uniform thickness and consistency of a skin, and is to offer the manufacture approach of a

reaction injection foaming article with good quality.
[0010]
[Means for Solving the Problem] While the above-mentioned purpose injects and carries out reaction semi-hardening of the reactant constituent undiluted solution of fizz into the mold for shaping, it is made to foam, and when the surface layer of this foaming object is in a semi-hardening condition, it can be attained by injecting the reactant constituent undiluted solution of non-fizz into the front face of the foaming object in a mold, and carrying out reaction hardening.
[0011] Hereafter, this invention is explained in detail, referring to a drawing. Drawing 1 is the explanatory view showing one embodiment of this invention. In drawing 1 , it is the mold for shaping of the sealing mating-die method with which the raw material tank with a heating jacket in which the temperature control of 10 and 20 is possible, and 30 have a mixing head, and 40 has a gas drainage hole, and is made possible by temperature control through warm water in the mold.
[0012] Moreover, the raw material tank with a heating jacket in which the temperature control of 50 and 60 is possible, and 70 are mixing heads, and are connected with the mold 40 for shaping like the above.
[0013] First, each component of the reactant constituent undiluted solution of fizz is breathed out from the raw material tanks 10 and 20. The reactant constituent undiluted solution of fizz is well-known, for example, the poly isocyanate and polyol which are described below are used as a principal component, and the thing which made the reactant constituent undiluted solution which comes to blend additives, such as a catalyst, a chain elongation agent, a cross linking agent, and other bulking agents, if needed contain a foaming agent is mainly used.
[0014] As poly isocyanate, tolylene diisocyanate (TDI, KURUDO TDI), diphenylmethane diisocyanate (MDI, a polymeric MDI, denaturation MDI), cyclo hexylmethane diisocyanate (hydrogenation MDI), etc. are mentioned.
[0015] Moreover, as polyol, polyester polyol, polyether polyol, aromatic amine system polyether polyol, etc. are mentioned. The hydroxyl value of polyols, such as this, has a desirable 350 - 700 mgKOH/g grade.
[0016] As a foaming agent, low-boiling point organic liquids and water, such as chlorofluocarbon (chlorofluocarbon 11, chlorofluocarbon 12, etc.), a methylene chloride, and ethylene chloride, are used. When using a low-boiling point organic liquid, this low-boiling point organic liquid gasifies with heating, and foams by this gas, but when using water as a foaming agent, this water reacts with the isocyanate radical of the above-mentioned poly isocyanate, carbon dioxide gas occurs, and it foams with this carbon dioxide gas.
[0017] Although based also on the expansion ratio of the foaming article which it is going to obtain, when the content of foaming agents, such as this, is generally used in the range of 5 - 20 weight section to the above-mentioned poly isocyanate 100 weight section when using a low-boiling point organic liquid as a foaming agent, and using water as a foaming agent, generally it is used in the range of 0.2 - 3 weight section to the above-mentioned poly isocyanate 100 weight section.
[0018] In addition, as a catalyst, an organic tin compound and an amine system catalyst are used, and additives, such as ****** for optimum dose and this, are also widely known for polyhydric alcohol and a multiple-valued amine as a chain elongation agent or a cross linking agent.
[0019] Since it is high activity chemically, just before usually main reactant components are prepared separately and injecting in the mold for shaping, such a reactant constituent undiluted solution of fizz mixes the reactant component which constitutes a reactant constituent undiluted solution, and is prepared.
[0020] For example, when using the poly isocyanate and polyol, the poly isocyanate is prepared for the raw material tank 10, and polyol is prepared for the raw material tank 20. By carrying out temperature control of the raw material tanks 10 and 20, heating maintenance of the raw materials, such as this, is usually carried out at the fixed temperature of about 20-40 degrees C.
[0021] And just before injecting in the mold 40 for shaping, this poly isocyanate and polyol are supplied to a mixing head 30, and collision mixing of each above-mentioned raw material by which heating maintenance was carried out at constant temperature is carried out. In this case, the above-mentioned

foaming agent and other additives are usually contained in the direction of a polyol component.
[0022] Subsequently, the reactant constituent undiluted solution of fizz mixed mixing HEDDODO 30 is immediately injected by the inside of the mold 40 for shaping of a sealing method, i.e., a cavity. In order to improve the fluidity within the mold of a reactant constituent undiluted solution, the mold 40 for shaping lets warm water pass in a mold, and heating maintenance is usually carried out at the fixed temperature of about 30-60 degrees C.
[0023] Each major component carries out reaction semi-hardening of the reactant constituent undiluted solution injected in the mold 40 for shaping, and it generates heat to coincidence with heat of reaction, and foams to it by the gas by the foaming agent, and a foaming object is formed. And it is cooled from the part which touches the internal surface of the mold 40 for shaping, and the surface layer of a semi-hardening condition is formed.
[0024] Thus, when the surface layer of a foaming object is in a semi-hardening condition, the reactant constituent undiluted solution of non-fizz is injected into the front face of the foaming object of the semi-hardening condition in a mold 40. If the timing which pours in the reactant constituent undiluted solution of non-fizz is too early, hardening is too slow, the reactant constituent undiluted solution of non-fizz enters to the interior of a foaming object, a good skin is not obtained, but hardening which is too slow conversely will progress too much, and adhesion with a foaming object and a skin will worsen.
[0025] A foaming agent is not used for the reactant constituent undiluted solution of the above-mentioned non-fizz in preparation of the reactant constituent undiluted solution of the above-mentioned fizz, but it is prepared like preparation of the reactant constituent undiluted solution of fizz except it.
[0026] In this case, the poly isocyanate and polyol are used as a principal component, and although the reactant constituent undiluted solution which blended additives, such as a catalyst, a chain elongation agent, a cross linking agent, and other bulking agents, and was prepared if needed is used suitably, the reactant constituent undiluted solution (thermosetting resin liquid) which uses a cyclopentadiene, a urea-resin, an epoxy resin, an unsaturated polyester resin, epoxy acrylate resin, urethane acrylate resin, etc. as a principal component can be used.
[0027] Generally, since reactant constituent undiluted solutions, such as this, are high activity chemically, main reactant components are prepared separately, and it is usually heated by 20-40 degrees C, and is breathed out from the raw material tanks 50 and 60, collision mixing is carried out by the mixing head 70, and they are immediately injected into the front face of the foaming object of the semi-hardening condition in the above-mentioned mold 40 for shaping after that, for example.
[0028] The reactant constituent undiluted solution of the above-mentioned non-fizz poured in into the mold 40 for shaping covers the foaming object (core layer) of a semi-hardening condition, and it is cooled from the part which touches the internal surface of the mold 40 for shaping, and the foaming object of the enveloping layer by the reactant constituent of non-fizz and a semi-hardening condition hardens, and is unified, and the foaming article with which the above-mentioned enveloping layer turned into a non-foaming skin is formed.
[0029] And after being cooled to the temperature which can be unmolded, without the foaming article in a mold deforming, it is unmolded by the conventional method. In this way, a foaming article like integral skin foam is obtained.
[0030] In addition, in an upper example, although the mold 40 for shaping of a sealing mating-die method was used, the mold for shaping of an open mating-die method can also be used. When using the mold for shaping of an open mating-die method, a mold is opened, the reactant constituent undiluted solution of non-fizz is poured in, a mold is closed after that, and the reactant constituent undiluted solution of non-fizz can be extended on the front face of the foam of a semi-hardening condition.
[0031] By the open mating-die method, the open mold must be gone up and down correctly, and leveling equipment is needed for a mold clamp machine. On the other hand, by the sealing mating-die method, although the high pressure injection machine more than clamping pressure is needed, since the clamping pressure at the time of shaping is comparatively low, by this invention, a sealing mating-die method is adopted suitably.
[0032]

[Function] While injecting and carrying out reaction semi-hardening of the reactant constituent undiluted solution of fizz into the mold for shaping, it is made to foam, and a non-foaming skin will be formed in the front face of the foaming object in a mold (core layer), if the reactant constituent undiluted solution of non-fizz is injected into the front face of the foaming object in a mold and reaction hardening is carried out, when the surface layer of this foaming object is in a semi-hardening condition.
[0033] And since the thickness of this skin can be adjusted thickly, thinly, and freely independently of the foaming object of that interior according to an injection rate and it moreover does not foam, there are no air bubbles and it becomes fixed [a consistency], and a delicate change of the skin which originates in air bubbles even if some dispersion is in the temperature of the mold for shaping does not take place, but dispersion in the thickness of a skin serves as homogeneity.
[0034]
[Example] Hereafter, the example and the example of a comparison of this invention are shown.
The reaction injection foaming article was manufactured by the approach shown in example 1 drawing 1 . Temperature control of the raw material tanks 10 and 20 was carried out to 40 degrees C, respectively, and the polyol (hydroxyl value 610 mgKOH/g) (SBU polyol H523: the Sumitomo Bayer make) which contains 0.6 % of the weight of water as a foaming agent heated by 40 degrees C from discharge and the raw material tank 20 in the denaturation diphenylmethane diisocyanate (28% of NCO components) (SBU isocyanate 0389: the Sumitomo Bayer make) heated by 40 degrees C from the raw material tank 10 was breathed out.
[0035] The regurgitation rate of each above-mentioned raw material was the denaturation diphenylmethane diisocyanate poly isocyanate 186 weight section to the polyol 100 weight section containing 0.6 % of the weight of water.
[0036] Then, collision mixing of each above-mentioned raw material was carried out by the mixing head 30, the reactant constituent undiluted solution of fizz was prepared, and the reactant constituent undiluted solution of this fizz was immediately injected in the mold 40 for shaping (cavity). Here, the temperature of the mold 40 for shaping carries out heating maintenance through warm water at 70 degrees C into a mold, and clamping pressure is 10 kg/cm2. It carried out.
[0037] It foams to the injected reactant constituent undiluted solution by the gas which occurs while carrying out reaction semi-hardening within the mold 40 for shaping, and the foaming object of a semi-hardening condition is formed in a mold. When the surface layer of this foaming object was in a semi-hardening condition, the reactant constituent undiluted solution of non-fizz was injected into the front face of the foaming object in a mold. Timing of impregnation was taken as the 45-second back of since the reactant constituent undiluted solution of fizz is injected in a mold 40.
[0038] The reactant constituent undiluted solution of non-fizz does not make the water which serves as a foaming agent in preparation in the reactant constituent undiluted solution of the above-mentioned fizz contain, but except it, is the same as the reactant constituent undiluted solution of fizz, and consists of denaturation diphenylmethane diisocyanate and polyol.
[0039] In this case, it carried out by making the denaturation diphenylmethane diisocyanate heated by 40 degrees C from the raw material tank 50 breathe out, and the polyol heated by 40 degrees C from the raw material tank 60 was made to breathe out, collision mixing of this was carried out by the mixing head 70, and it poured into the front face of the foaming object in a mold 40 immediately after that.
[0040] The reactant constituent undiluted solution of the above-mentioned non-fizz poured in into the mold 40 for shaping covered the foaming object of a semi-hardening condition, and it was cooled from the part which touches the internal surface of the mold 40 for shaping, and the foaming object of the enveloping layer by the reactant constituent of non-fizz and a semi-hardening condition hardened, and was unified, and the foaming article with which the above-mentioned enveloping layer turned into a non-foaming skin was formed.
[0041] Since unmolding of the above-mentioned foaming article of the semi-hardening condition which became an elevated temperature with reaction heat of hardening was attained without being cooled with the mold 40 for shaping held at 70 degrees C, and the foaming article in a mold deforming after [of impregnation of the reactant constituent undiluted solution of non-fizz] 7 minutes and 15 seconds, it

was unmolded with the conventional method and obtained the foaming article.
[0042] The obtained foaming article (rectangle) was good integral skin foam which consists of a skin (about 2.1mm in thickness, and consistency about 1.1 g/cm3), and a foaming layer (about 8mm in thickness, and consistency about 0.6 g/cm3) it is [layer] full of the interior of this skin.
[0043] In order to evaluate dispersion in the thickness of the skin of the above-mentioned foaming article (rectangle), when the thickness of the skin of the four-corners part of a foaming article and a central part was measured correctly, four-corners parts were 2.1mm, 2.1mm, 2.1mm, and 2.1mm, the central part was 2.2mm and the skin was thickly [comparatively] uniform.
[0044] The reaction injection foaming article was manufactured by the approach of example of comparison 1 citation given in JP,63-24448,B. In this approach, temperature control of the raw material tanks 10 and 20 and the mixing head 30 was carried out to 40 degrees C, respectively, and the temperature of the reactant constituent undiluted solution of the same fizz as an example 1 was heated at 40 degrees C. In addition, the reactant constituent undiluted solution of non-fizz was not used, therefore the raw material tanks 50 and 60 and a mixing head 70 did not use it.
[0045] And the temperature of the mold 40 for shaping was adjusted through 70-degree C warm water in the same mold 40 for shaping as an example 1, the 40 above-mentioned degrees C reactant constituent undiluted solution was injected in this mold 40 for shaping, and reaction hardening and foaming of a reactant constituent undiluted solution were performed. And after [of injection] 4 minutes, the mold 40 for shaping was switched to 10-degree C cold water from 70-degree C warm water, and it cooled.
[0046] Since unmolding became possible, without the foaming article in a mold deforming (after [of injection] 8 minutes) 4 minutes after switching to 10-degree C cold water, it unmolded with the conventional method and the foaming article was obtained.
[0047] The obtained foaming article (rectangle) was good integral skin foam which consists of a skin and a foaming layer it is [layer] full of the interior of this skin like an example 1 seemingly.
[0048] However, the four-corners parts of dispersion in the thickness of the skin of the above-mentioned foaming article (rectangle) were 2.0mm, 2.0mm, 1.7mm, and 2.2mm, the central part was 1.8mm and the skin was uneven compared with the example 1.
[0049] In the example of comparison 2 this gentleman method, temperature control of the raw material tanks 10 and 20 and the mixing head 30 was carried out to 40 degrees C, respectively, and the temperature of the reactant constituent undiluted solution of the same fizz as an example 1 was heated at 40 degrees C. In addition, the reactant constituent undiluted solution of non-fizz was not used, therefore the raw material tanks 50 and 60 and a mixing head 70 did not use it.
[0050] And the temperature of the mold 40 for shaping was adjusted through 70-degree C warm water in the same mold 40 for shaping as an example 1, the 40 above-mentioned degrees C reactant constituent undiluted solution was injected in this mold 40 for shaping, and reaction hardening and foaming of a reactant constituent undiluted solution were performed.
[0051] Since unmolding became possible after [of injection] 10 minutes, without the foaming article in a mold deforming, it unmolded with the conventional method and the foaming article was obtained.
[0052] The obtained foaming article (rectangle) was good integral skin foam which consists of a skin and a foaming layer it is [layer] full of the interior of this skin like an example 1 seemingly.
[0053] However, the four-corners parts of dispersion in the thickness of the skin of the above-mentioned foaming article (rectangle) were 1.1mm, 1.3mm, 1.3mm, and 1.4mm, the central part was 0.8mm and the skin was thinly uneven compared with the example 1.
[0054]
[Effect of the Invention] As above-mentioned, the manufacture approach of the reaction injection foaming article this invention It is what it is made to foam while injecting and carrying out reaction semi-hardening of the reactant constituent undiluted solution of fizz into the mold for shaping, and the reactant constituent undiluted solution of non-fizz is injected [what] into the front face of the foaming object in a mold, and carries out reaction hardening when the surface layer of this foaming object is in a semi-hardening condition. Thereby, the thickness and the consistency of a skin are uniform and a reaction injection foaming article with good quality can be obtained.

[0055] Moreover, according to this invention, by adjusting the injection rate of the reactant constituent undiluted solution of non-fizz, ****** which adjusts the thickness of a skin easily and to burn is made, and there is an advantage that a foaming article with high reinforcement can be manufactured, by thickening thickness of a skin.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the explanatory view showing one embodiment of this invention.
[Description of Notations]
10 Raw Material Tank for Reactant Constituent Undiluted Solutions of Fizz
20 Raw Material Tank for Reactant Constituent Undiluted Solutions of Fizz
30 Mixing Head for Reactant Constituent Undiluted Solutions of Fizz
40 Molding Die
50 Raw Material Tank for Reactant Constituent Undiluted Solutions of Non-Fizz
60 Raw Material Tank for Reactant Constituent Undiluted Solutions of Non-Fizz
70 Mixing Head for Reactant Constituent Undiluted Solutions of Non-Fizz

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[Translation done.]

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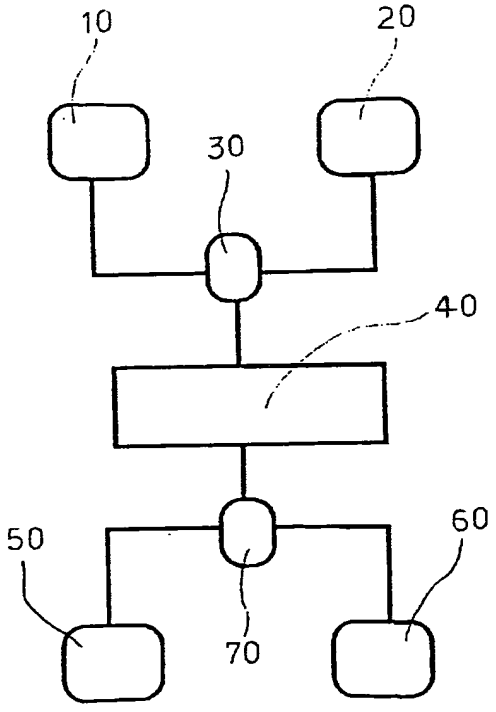
(54)【発明の名称】　反応射出発泡成形品の製造方法

(57)【要約】

【目的】　スキン層の厚さ及び密度が均一で、品質良好な反応射出発泡成形品を得る。

【構成】　発泡性の反応性組成物原液を成形用型内に射出し反応半硬化させるとともに発泡させ、この発泡成形体の表面層が半硬化状態の時に、型内の発泡成形体の表面に非発泡性の反応性組成物原液を注入し反応硬化させることによって、目的の反応射出発泡成形品を得る。



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【特許請求の範囲】

【請求項１】　発泡性の反応性組成物原液を成形用型内に射出し反応半硬化させるとともに発泡させ、この発泡成形体の表面層が半硬化状態の時に、型内の発泡成形体の表面に非発泡性の反応性組成物原液を注入し反応硬化させることを特徴とする反応射出発泡成形品の製造方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】この発明は、インテグラルスキンフォームのような反応射出発泡成形品の製造方法に関する。

【０００２】

【従来の技術】発泡性の反応性組成物原液を成形用型内に射出し反応硬化させて、インテグラルスキンフォーム（スキン層付きフォーム）のような反応射出発泡成形品を製造する方法は知られている。

【０００３】この種の反応射出発泡成形品の製造方法にあっては、反応性組成物原液の型内での流動性を良くするために、成形用型は通常３０～６０℃に加熱保持される。一方、反応性組成物原液は反応硬化時に発熱して型温度よりも高温（例えば、ウレタンフォーム成形の場合は１００℃程度）になる。

【０００４】そして、発泡剤含有の反応性組成物原液は反応硬化とともに発泡し型に接する部分から冷却され、それにより型に接する部分に形成される気泡膜内のガスが冷却されて凝縮し、この部分の気泡膜が萎縮して高密度のスキン層が形成され、その後発泡成形品が脱型可能な温度まで冷却されて脱型される。

【０００５】しかし、このように成形用型の温度が３０～６０℃の一定温度に保持された状態で発泡成形品が冷却される場合は、型内の発泡成形品の温度を脱型可能な温度まで下げるのに時間がかかり生産性が低い。

【０００６】また、形成されるスキン層は比較的薄く（約１㎜ぐらい）、しかもその密度も比較的小さく、そのため得られる発泡成形品に強度が弱く、充分に満足のいく製品は得られない。

【０００７】そこで、脱型するまでの時間を短縮して生産性を向上させ、高強度の発泡成形品を得るために、成形用型を一定温度に加熱して反応性組成物原液を反応硬化させた後、この成形用型を急冷することによりスキン層の厚さ及び密度を制御する方法が提案されている（特公昭６３－２４４４８号公報参照）。

【０００８】

【発明が解決しようとする課題】ところが、上記提案の方法では、スキン層の厚さは増加するが、成形用型にはどうしても温度分布のばらつきがあり、この温度分布のばらつきに起因してスキン層に存在するわずかの気泡が微妙に変化するため、スキン層の厚さ及び密度が不均一となるという問題がある。

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【０００９】この発明は、上記の問題を解決するもので、その目的とするところは、スキン層の厚さ及び密度が均一で、品質良好な反応射出発泡成形品の製造方法を提供することにある。

【００１０】

【課題を解決するための手段】上記の目的は、発泡性の反応性組成物原液を成形用型内に射出し反応半硬化させるとともに発泡させ、この発泡成形体の表面層が半硬化状態の時に、型内の発泡成形体の表面に非発泡性の反応性組成物原液を注入し反応硬化させることによって達成することができる。

【００１１】以下、図面を参照しながら、この発明を詳しく説明する。図１はこの発明の一実施態様を示す説明図である。図１において、１０及び２０は温調可能な加熱ジャケット付きの原料タンク、３０はミキシングヘッド、４０はガス抜き孔を有する密閉合せ型方式の成形用型で、型内に温水を通して温調可能になされている。

【００１２】また、５０及び６０は温調可能な加熱ジャケット付きの原料タンク、７０はミキシングヘッドであり、上記と同様に成形用型４０へ連結されている。

【００１３】先ず、原料タンク１０及び２０から発泡性の反応性組成物原液の各成分が吐出される。発泡性の反応性組成物原液は公知のもので、例えば、以下に述べるポリイソシアネートとポリオールとを主成分とし、必要に応じて触媒、鎖延長剤、架橋剤、その他充填剤等の添加剤を配合してなる反応性組成物原液に、発泡剤を含有させたものが主に用いられる。

【００１４】ポリイソシアネートとしては、トリレンジイソシアネート（ＴＤＩ、クルードＴＤＩ）、ジフェニルメタンジイソシアネート（ＭＤＩ、ポリメリックＭＤＩ、変性ＭＤＩ）、シクロヘキシルメタンジイソシアネート（水添ＭＤＩ）等が挙げられる。

【００１５】また、ポリオールとしては、ポリエステルポリオール、ポリエーテルポリオール、芳香族アミン系ポリエーテルポリオール等が挙げられる。これ等のポリオールの水酸基価は３５０～７００ ｍｇＫＯＨ／ｇ程度が好ましい。

【００１６】発泡剤としては、フロン（フロン１１、フロン１２など）、メチレンクロライド、エチレンクロライド等の低沸点有機液体や水が用いられる。低沸点有機液体を用いる場合は、この低沸点有機液体が加熱によりガス化し、このガスによって発泡するが、水を発泡剤として用いる場合は、この水が上記ポリイソシアネートのイソシアネート基と反応して炭酸ガスが発生し、この炭酸ガスによって発泡する。

【００１７】これ等の発泡剤の含有量は、得ようとする発泡成形品の発泡倍率にもよるが、発泡剤として低沸点有機液体を用いる場合は、一般に上記ポリイソシアネート１００重量部に対して５～２０重量部の範囲で用いられ、発泡剤として水を用いる場合は、上記ポリイソシア

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ネート１００重量部に対して一般に０．２～３重量部の範囲で用いられる。

【００１８】なお、触媒としては有機錫化合物やアミン系触媒が用いられ、鎖延長剤や架橋剤としては多価アルコール類や多価アミンが適量用いられ、これ等の添加剤も広く知られている。

【００１９】このような発泡性の反応性組成物原液は、化学的に高活性であるので、通常は主要な反応性成分が別々に用意され、成形用型内に射出する直前に、反応性組成物原液を構成する反応性成分を混合して調製される。

【００２０】例えば、ポリイソシアネートとポリオールとを用いる場合、原料タンク１０にポリイソシアネートが用意され、原料タンク２０にポリオールが用意される。これ等の原料は原料タンク１０及び２０を温調することにより、通常２０～４０℃程度の一定の温度に加熱保持される。

【００２１】そして、一定温度に加熱保持された上記各原料は、成形用型４０内に射出する直前に、このポリイソシアネートとポリオールとがミキシングヘッド３０に供給され衝突混合される。この場合、上記発泡剤及びその他の添加剤は、通常ポリオール成分の方に含有される。

【００２２】次いで、ミキシングヘッドド３０混合された発泡性の反応性組成物原液は、直ちに密閉方式の成形用型４０内、すなわちキャビティに射出される。成形用型４０は、反応性組成物原液の型内での流動性を良くするために、型内に温水を通して、通常３０～６０℃程度の一定の温度に加熱保持される。

【００２３】成形用型４０内に射出された反応性組成物原液は、各主要成分が反応半硬化し、同時に反応熱により発熱して発泡剤によるガスにより発泡し発泡成形体が形成される。そして、成形用型４０の内壁面に接する部分から冷却されて半硬化状態の表面層が形成される。

【００２４】このように発泡成形体の表面層が半硬化状態の時に、型４０内の半硬化状態の発泡成形体の表面に非発泡性の反応性組成物原液が注入される。非発泡性の反応性組成物原液を注入するタイミングは、あまりにも早すぎると硬化が遅すぎて発泡成形体の内部まで非発泡性の反応性組成物原液が入り込み良好なスキン層が得られず、逆にあまりにも遅すぎる硬化が進みすぎて発泡成形体とスキン層との密着が悪くなる。

【００２５】上記非発泡性の反応性組成物原液は、前述の発泡性の反応性組成物原液の調製において発泡剤を使用せず、それ以外は発泡性の反応性組成物原液の調製と同様にして調製される。

【００２６】この場合、ポリイソシアネートとポリオールとを主成分とし、必要に応じて触媒、鎖延長剤、架橋剤、その他充填剤等の添加剤を配合して調製された反応性組成物原液が好適に用いられるが、その他シクロペンタジエン、尿素樹脂、エポキシ樹脂、不飽和ポリエステル樹脂、エポキシアクリレート樹脂、ウレタンアクリレート樹脂等を主成分とする反応性組成物原液（熱硬化性樹脂液）を用いることができる。

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【００２７】これ等の反応性組成物原液は、一般に化学的に高活性であるので、例えば、主要な反応性成分が別々に用意され、通常２０～４０℃に加熱され原料タンク５０及び６０から吐出され、ミキシングヘッド７０で衝突混合され、その後直ちに上記成形用型４０内の半硬化状態の発泡成形体の表面に注入される。

【００２８】成形用型４０内に注入された上記非発泡性の反応性組成物原液は、半硬化状態の発泡成形体（コア層）を覆い、成形用型４０の内壁面に接する部分から冷却されて、非発泡性の反応性組成物による被覆層及び半硬化状態の発泡成形体が硬化し一体化され、上記被覆層が非発泡のスキン層となった発泡成形品が形成される。

【００２９】そして、型内の発泡成形品が変形せずに脱型可能な温度まで冷却された後、常法により脱型される。こうして、インテグラルスキンフォームのような発泡成形品が得られる。

【００３０】なお、上例においては、密閉合せ型方式の成形用型４０を用いたが、開放合せ型方式の成形用型を用いることもできる。開放合せ型方式の成形用型を用いる場合は、型を開いて非発泡性の反応性組成物原液を注入し、その後型を閉じて非発泡性の反応性組成物原液を半硬化状態の発泡体の表面に押し広げられる。

【００３１】開放合せ型方式では、開いた型を正確に上下せねばならず、型締め機にレベリング装置が必要となる。一方、密閉合せ型方式では、型締め圧以上の高圧注入機が必要になるが、この発明では成形時の型締め圧が比較的低いので、密閉合せ型方式が好適に採用される。

【００３２】

【作用】発泡性の反応性組成物原液を成形用型内に射出し反応半硬化させるとともに発泡させ、この発泡成形体の表面層が半硬化状態の時に、型内の発泡成形体の表面に非発泡性の反応性組成物原液を注入し反応硬化させると、型内の発泡成形体（コア層）の表面に非発泡のスキン層が形成される。

【００３３】そして、このスキン層の厚みは、その内部の発泡成形体から独立して、注入量に応じて厚くも薄くも自由に調節することができ、しかも非発泡であるので気泡は全くなく密度は一定となり、成形用型の温度に多少のばらつきがあっても気泡に起因するスキン層の微妙な変化は起こらず、スキン層の厚みのばらつきが均一となる。

【００３４】

【実施例】以下、この発明の実施例及び比較例を示す。

実施例１

図１に示す方法で反応射出発泡成形品を製造した。原料タンク１０及び２０をそれぞれ４０℃に温調し、原料タ

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ンク１０から４０℃に加熱された変性ジフェニルメタンジイソシアネート（ＮＣＯ成分２８％）（ＳＢＵイソシアネート０３８９：住友バイエル社製）を吐出し、原料タンク２０から４０℃に加熱された発泡剤として水０．６重量％を含有するポリオール（水酸基価６１０ ｍｇＫＯＨ／ｇ）（ＳＢＵポリオールＨ５２３：住友バイエル社製）を吐出した。

【００３５】上記各原料の吐出割合は、水０．６重量％を含有するポリオール１００重量部に対して、変性ジフェニルメタンジイソシアネートポリイソシアネート１８６重量部であった。

【００３６】その後、上記各原料をミキシングヘッド３０で衝突混合して、発泡性の反応性組成物原液を調製し、この発泡性の反応性組成物原液を直ちに成形用型４０内（キャビティ）に射出した。ここで、成形用型４０の温度は型内に温水を通して７０℃に加熱保持し、型締め圧は１０ ｋｇ／ｃｍ² とした。

【００３７】射出した反応性組成物原液は、成形用型４０内で反応半硬化するとともに発生するガスにより発泡し、型内に半硬化状態の発泡成形体が形成される。この発泡成形体の表面層が半硬化状態の時に、型内の発泡成形体の表面に非発泡性の反応性組成物原液を注入した。注入のタイミングは、発泡性の反応性組成物原液を型４０内に射出してから４５秒後とした。

【００３８】非発泡性の反応性組成物原液は、上記発泡性の反応性組成物原液を調製において、発泡剤となる水を含有させず、それ以外は発泡性の反応性組成物原液と同じで、変性ジフェニルメタンジイソシアネートとポリオールとからなる。

【００３９】この場合、原料タンク５０から４０℃に加熱された変性ジフェニルメタンジイソシアネートを吐出させし、原料タンク６０から４０℃に加熱されたポリオールを吐出させ、これをミキシングヘッド７０により衝突混合し、その後直ちに型４０内の発泡成形体の表面に注入した。

【００４０】成形用型４０内に注入された上記非発泡性の反応性組成物原液は、半硬化状態の発泡成形体を覆い、成形用型４０の内壁面に接する部分から冷却されて、非発泡性の反応性組成物による被覆層及び半硬化状態の発泡成形体が硬化し一体化され、上記被覆層が非発泡のスキン層となった発泡成形品が形成された。

【００４１】反応硬化熱によって高温になった半硬化状態の上記発泡成形品は、７０℃に保持された成形用型４０により冷却され、非発泡性の反応性組成物原液の注入から7分１５秒後には型内の発泡成形品が変形せずに脱型可能になったので、常法により脱型して発泡成形品を得た。

【００４２】得られた発泡成形品（長方形）は、スキン層（厚さ約２．１㎜、密度約１．１ｇ／ｃｍ³ ）と、このスキン層の内部に充満する発泡層（厚さ約８㎜、密度約

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０．６ｇ／ｃｍ³ ）とからなる良好なインテグラルスキンフォームであった。

【００４３】上記発泡成形品（長方形）のスキン層の厚みのばらつきを評価するために、発泡成形品の四隅部分と中央部分とのスキン層の厚みを正確に測定したところ、四隅部分は２．１㎜、２．１㎜、２．１㎜、２．１㎜で、中央部分は２．２㎜であり、スキン層は比較的厚く且つ均一であった。

【００４４】比較例１

引用の特公昭６３－２４４４８号公報記載の方法で反応射出発泡成形品を製造した。この方法においては、原料タンク１０及び２０、ミキシングヘッド３０をそれぞれ４０℃に温調して、実施例１と同じ発泡性の反応性組成物原液の温度を４０℃に加熱した。なお、非発泡性の反応性組成物原液は使用せず、したがって原料タンク５０及び６０、ミキシングヘッド７０は使用しなかった。

【００４５】そして、実施例１と同様な成形用型４０に７０℃の温水を通して成形用型４０の温度を調節し、この成形用型４０内に上記４０℃の反応性組成物原液を射出して、反応性組成物原液の反応硬化と発泡とを行った。そして、射出から４分後に、成形用型４０を７０℃の温水から１０℃の冷水に切り換えて冷却した。

【００４６】１０℃の冷水に切り換えてから４分後（射出から８分後）には、型内の発泡成形品が変形せずに脱型可能となったので、常法により脱型して発泡成形品を得た。

【００４７】得られた発泡成形品（長方形）は、見掛け上は実施例１と同様に、スキン層と、このスキン層の内部に充満する発泡層とからなる良好なインテグラルスキンフォームであった。

【００４８】しかし、上記発泡成形品（長方形）のスキン層の厚みのばらつきは、四隅部分は２．０㎜、２．０㎜、１．７㎜、２．２㎜で、中央部分は１．８㎜であり、スキン層は実施例１に比べて不均一であった。

【００４９】比較例２

この方法においては、原料タンク１０及び２０、ミキシングヘッド３０をそれぞれ４０℃に温調して、実施例１と同じ発泡性の反応性組成物原液の温度を４０℃に加熱した。なお、非発泡性の反応性組成物原液は使用せず、したがって原料タンク５０及び６０、ミキシングヘッド７０は使用しなかった。

【００５０】そして、実施例１と同様な成形用型４０に７０℃の温水を通して成形用型４０の温度を調節し、この成形用型４０内に上記４０℃の反応性組成物原液を射出して、反応性組成物原液の反応硬化と発泡とを行った。

【００５１】射出から１０分後には、型内の発泡成形品が変形せずに脱型可能となったので、常法により脱型して発泡成形品を得た。

【００５２】得られた発泡成形品（長方形）は、見掛け

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上は実施例１と同様に、スキン層と、このスキン層の内部に充満する発泡層とからなる良好なインテグラルスキンフォームであった。

【００５３】しかし、上記発泡成形品（長方形）のスキン層の厚みのばらつきは、四隅部分は１．１㎜、１．３㎜、１．３㎜、１．４㎜で、中央部分は０．８㎜であり、スキン層は実施例１に比べて薄く且つ不均一であった。

【００５４】

【発明の効果】上述の通り、この発明の反応射出発泡成形品の製造方法は、発泡性の反応性組成物原液を成形用型内に射出し反応半硬化させるとともに発泡させ、この発泡成形体の表面層が半硬化状態の時に、型内の発泡成形体の表面に非発泡性の反応性組成物原液を注入し反応硬化させるもので、それによりスキン層の厚さ及び密度が均一で、品質良好な反応射出発泡成形品を得ることができる。

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【００５５】また、この発明によれば、非発泡性の反応性組成物原液の注入量を調節することにより、スキン層の厚さを容易に調節するこがすることができ、スキン層の厚さを厚くすることにより、強度が高い発泡成形品を製造することができるという利点がある。

【図面の簡単な説明】

【図１】この発明の一実施態様を示す説明図である。

【符号の説明】

１０　発泡性の反応性組成物原液用の原料タンク
２０　発泡性の反応性組成物原液用の原料タンク
３０　発泡性の反応性組成物原液用のミキシングヘッド
４０　成形用金型
５０　非発泡性の反応性組成物原液用の原料タンク
６０　非発泡性の反応性組成物原液用の原料タンク
７０　非発泡性の反応性組成物原液用のミキシングヘッド

【図１】